NASA-TM-111570

Morphology of Thermoset Polyimides by Positron Annihilation Spectroscopy

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Presented at
61st Meeting of the Southeastern Section
of the American Physical Society
held at
Newport News, VA
Nov. 10-12, 1994

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ABSTRACT

Thermoset polyimides have great potential for successfully meeting tough stress and temperature challenges in the advanced aircraft development program. However, studies of structure/property relationships in these materials have not been very successful so far. Positron Annihilation Spectroscopy has been used to investigate free volumes and associated parameters. It has been noted that the free volume correlates well with the molecular weight, cross-link density and thermal coefficient of expansion of these materials. Currently no other techniques are available for direct measurement of these parameters. Experimental results and their interpretations will be discussed.

INTRODUCTION

The new generation of supersonic transport aircraft must have a useful life of about 60,000 hours, 75% of which will be at supersonic speeds and hence high temperatures. Graphite fiber/polymer matrix composites have a high potential for successfully meeting the high stress/temperature challenges expected for the new generation of high speed aircraft. They can operate successfully upto 600° F, have superior corrosion resistance, excellent chemical resistance, good dimensional stability and good dielectric properties. However, definitive studies of structure/property relations in these materials have not yet been made. Our preliminary studies of selected candidate composite materials had indicated that thermoset polyimides may provide better matrix material than thermoplastic polyimides.

It was therefore decided to conduct a detailed study of microstructural characteristics of a recently developed[1] thermoset polyimide resin. The long term thermal aging effects in these polymers are expected[2] to be strongly related to their cross-link densities. According to kinetic theory[3] of rubber elasticity, the cross-link density(ν) is inversely related to the average molecular weight (M_c) between the cross-links. We have previously established direct correlation between molecular weight and free volume cell size in linear polymers[4] and dielectric constant and free volume fractions in polyimide films[5]. These studies clearly established that the physical/electrical properties of polymeric materials are strongly dependent on their molecular architecture. It was therefore felt desirable to measure free volume cell size (V_f) in a series of variable segmental molecular weight polyimide samples in order to develop a direct correlation between V_f and the cross-link density. The free volume cell sizes have also been correlated with the thermal coefficient of expansion (TCE) of these samples. The experimental techniques and the results of these measurements are described in the following sections.

EXPERIMENTAL TECHNIQUES

1.Sample preparation:

The high temperature LaRC™-46 series polyimide resins were prepared from three monomer reactants: the monomethyl ester of 5-norbornen-2,3'-dicarboxylic acid(NE), dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid(BTDE) and 3,4'-oxydianiline(3,4'-ODA). Five resin systems were synthesized in which the formulated molecular weight (FMWT) between the crosslink sites varied from 1500 to 21000. The monomer reactants were dissolved in methanol to give a 50% by weight monomeric

solution. The monomeric solution was concentrated in a vacuum oven at 250°C for 1 hour to yield an imidized prepolymer. The pre imized oligomer was finally cured at 325°C for 1 hour under pressure.

The formulated molecular weight (FMWT) of the resin samples was calculated as follows: FMWT = n molecular weight (MWT) of BTDE + (n+1) MWT of (3,4'-ODA) + 2 MWT of NE - 2(n+1)(MWT of H_2O + MWT of CH_3OH), where n is the molar ratio for the monomer reactants and by-products formed during the imidization.

The samples used in positron lifetime measurements were in the form of discs of thickness varying from 1mm to 4mm. X-ray diffraction measurements in the test samples showed that all of them were almost totally amorphous.

2. Free volume measurements:

Positron lifetime measurements have been carried out using a conventional fast-fast coincidence system with a time resolution of about 280 ps. A 25 μCi ^{22}Na source deposited on a 8.46 μm thick kapton foil, sandwiched between two discs of the sample, was located between the start and stop plastic scintillation detectors . Positron lifetimes were measured at room temperature and at ambient pressure. Several measurements were made with each sample in order to check the reproducibility of the spectrometer. Normally each spectrum contained more than 10^6 counts under the spectrum accumulated in approximately 8 hours.

The measured lifetime spectra were analyzed using the computer program PATFIT88[6]. Two lifetime component analysis invariably gave large χ^2 values. We tried three lifetime component fits which resulted in lower χ^2, but the intensity of the third

lifetime component was negligible (< 0.5%).This indicates that the sizes of the microvoids or free volume cells are too small for the formation and localization of positronium atoms. Therefore, the second lifetime component (τ_2) from the three component analysis, which is due to the positron annihilation at the defect sites in the resin matrix, is used to calculate the microvoid "size" in present series of samples. A typical positron lifetime spectrum in a resin sample is shown in fig.1

3. Thermal coefficient of expansion measurement:

Density of each of the resin samples was measured using a Troemner specific gravity chain balance system and a graduated cylinder filled with distilled water. Densities of the samples are needed for calculating their cross-link densities. Thermal coefficient of expansion of the resin samples were measured by measuring the sample volumes at two different temperatures. These measurements were made with the same Troemner balance that was used for the sample density measurements. Measurements were repeated several times to get consistent results. Samples were desiccated before the start of each repeat measurement. The physical properties of the resin are summarized in Table 1.and the lifetime results are presented in Table 2.

EXPERIMENTAL RESULTS

The second lifetime component in each of the samples corresponds to the positrons trapped at the potential defects(free volume cells) in the resin matrix. These free volume cells result from fluctuations in the packing density and morphology of the macromolecular chains. As pointed out earlier, the sizes of these free volume cells are too small for the formation of positronium, the bound state of positron-electron pair. Therefore the positrons

are potentially trapped at these smaller free volume cells and subsequently annihilate there. The radii R (in nanometers) of the free volume cells and the trapped positron lifetime τ_2 (in nanoseconds) are related as follows [4]:

$$\frac{1}{4\tau_2} = 1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi} Sin \frac{2\pi R}{R+\Delta R} \qquad (1)$$

where $\Delta R = 0.1659$ nanometers.

This equation differs from the conventional model[7] for positronium forming media in having $1/4\tau_2$ in place of $1/2\tau_3$ on the left hand side. A detailed discussion of this modification of the conventional relation can be found in ref.4. The free volume cell size V_{f2} is calculated as $(4/3)\pi R^3$.

The cross-link density (ν) and the molecular weight (M_c) of the polymers are inversely related according to the kinetic theory of rubber elasticity[3].

$$\nu = A\frac{\rho}{M_c} \qquad (2)$$

where A is the Avogadro number and ρ is the resin density.

Using the measured density and average molecular weight between the cross-links of the samples, the cross-link density was calculated. These values along with the calculated free volume cell size V_{f2} and thermal coefficient of expansion data are summarized in table 3. Figures 2,3 and 4 show the correlation between free volume cell size V_{f2} and molecular weight M_c, free volume cell size and cross-link density ν, and free volume cell size and thermal coefficient of expansion (CTE) respectively.

DISCUSSION

It is clear from the data presented in table 3 and illustrated in figs.2-3 that the free volume cell size correlates well with the segmental molecular weight and the cross-link density of the resins. By extending the free volume model of Singh and Eftekhari[4] to the cross linked thermoset polyimide resins, we find that free volume size and molecular weight are related by a similar expression i.e.,

$$V_{f2}=AM_c^B \tag{3}$$

where $A=5.37\pm0.11$ and $B=0.037\pm0.002$.

The exponent B is rather small in comparison with that for linear polymers and epoxies investigated earlier in this laboratory. However, it still estimates the molecular weight of the solid polymers(resins) reasonably well in the mass range of 1500 to 21000 (g/mol). It is interesting to find that the correlation between free volume and cross link density (ν) fits into similar relation, as expected, since cross link density is inversely proportional to molecular weight i.e.,

$$V_{f2}=A_1\upsilon^{-B_1} \tag{4}$$

where $A_1 = 47.13\pm0.94$ and $B_1 = 0.04\pm0.002$.

The cross-link density is known to significantly affect many of the physical and mechanical properties of cross-linked systems. Hence accurate experimental measurement of this quantity is important. Most of the currently available methods for calculating cross-link density require the polymer system to be in equilibrium in a liquid solution. A

simple relation of the type (4) shows that by measuring the free volume size by positron annihilation technique, cross-link density of the sample can be readily obtained without dissolving the sample in an appropriate solvent. A new dimension to the present set of measurements is added if we examine the relation between V_{f2} and CTE. Although the experimental results are rather scattered, they still follow the trend which fits into a relation of the following type

$$V_{f2}=A_2(CTE)^{B_2} \tag{5}$$

where $A_2=14.03\pm0.71$ and $B_2=0.076\pm0.003$.

From fig.4 it is clear that CTE increases with increasing free volume cell size. This trend is expected since the sample porosity, given by $kV_{f2}I_2$, where k is a structural constant and I_2 is the percentage of the area under the second lifetime component, is expected to be proportional to V_{f2}. This is very well reflected in Figure 5. The porosity, in turn, is directly proportional to coefficient of thermal expansion. Therefore free volume cell size turns out to be a unique parameter whose measurement should enable one to estimate other material properties, such as M_c, ν and CTE, at least in the segmental molecular weight range of 1500 tp 21000 g/mol.

CONCLUDING REMARKS

It has been demonstrated that free volume cell size in thermoset polyimides is a versatile parameter. It relates directly to the segmental molecular weight, cross-link density and thermal coefficient of expansion of the test samples. Thus a single measurement of free volume cell size provides a viable basis for microstructural characterization of thermoset

polyimides. The product of free volume cell size and the relative intensity of its associated lifetime component, which is proportional to the porosity of the sample, provides a direct indication of its dimensional stability under thermal and mechanical loads.

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Table 1. Physical properties of test polyimide resins

Sample	Density (g/cm^3)	Segmental Mol.Weight (g/mol)
RP-46-5	1.36	1500
RP-51	1.40	9000
RP-67T-1	1.47	10000
RP-47	1.37	15000
RP-49-2	1.35	21000

Table 2. Summary of positron lifetimes in polyimide resin samples

Sample	τ_1 (psec)	τ_2 (psec)	τ_3 (psec)	I_1 (%)	I_2 (%)	I_3 (%)
RP-46-5	138 ±8	379 ± 1	2011± 230	17± 1	82 ± 1	<0.5
RP-51	114 ±5	383 ± 2	2400± 200	19± 1	80 ± 1	<0.5
RP-67T-1	138 ±8	384 ± 2	2347± 213	17±1	82 ± 1	<0.5
RP-47	129±10	385 ± 1	2619± 394	16±1	83 ± 1	<0.5
RP-49-2	145±10	387 ± 1	2449± 269	16±1	83 ± 1	<0.5

Table 3. Summary of free volume, cross-link density and CTE results

Sample	V_{f2} (Å^3)	ν (cls/cm^3) x10^{19}	CTE (x 10^{-4}/°C)
RP-46-5	7.04±0.1	54.50±5	1.26
RP-51	7.54±0.1	9.37±0.9	2.25
RP-67T-1	7.56±0.1	8.86±0.9	4.39
RP-47	7.58±0.1	5.37±0.5	2.14
RP-49-2	7.78±0.1	3.87±0.4	4.85

Note: CTE values have ± 5% error

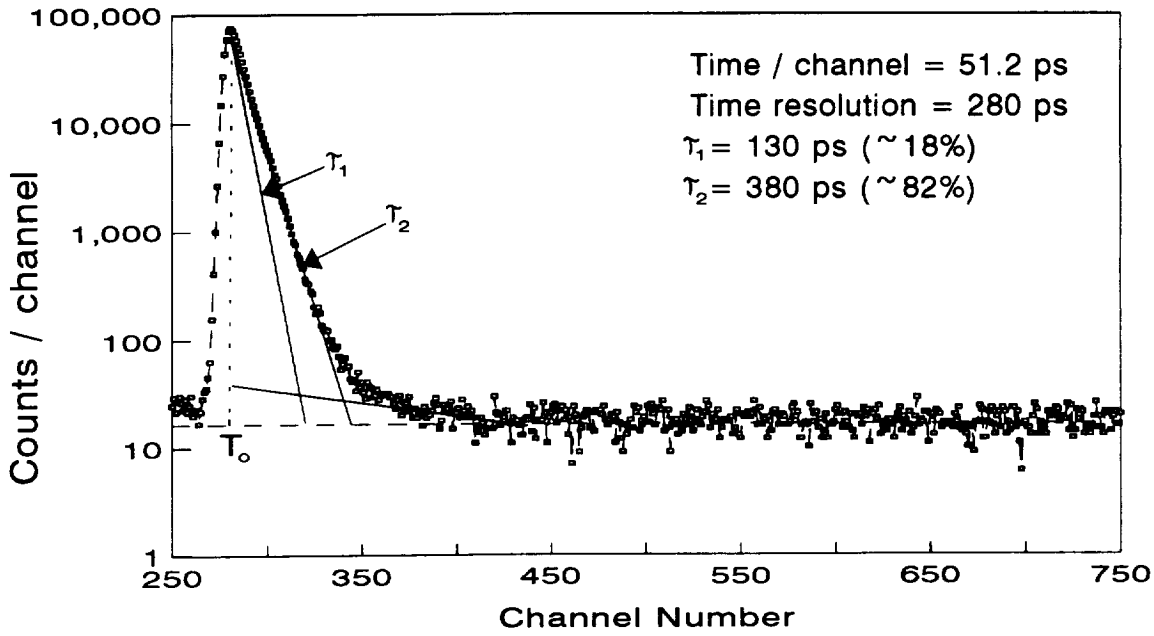

Fig.1. A typical positron lifetime spectrum in RP46 resin sample.

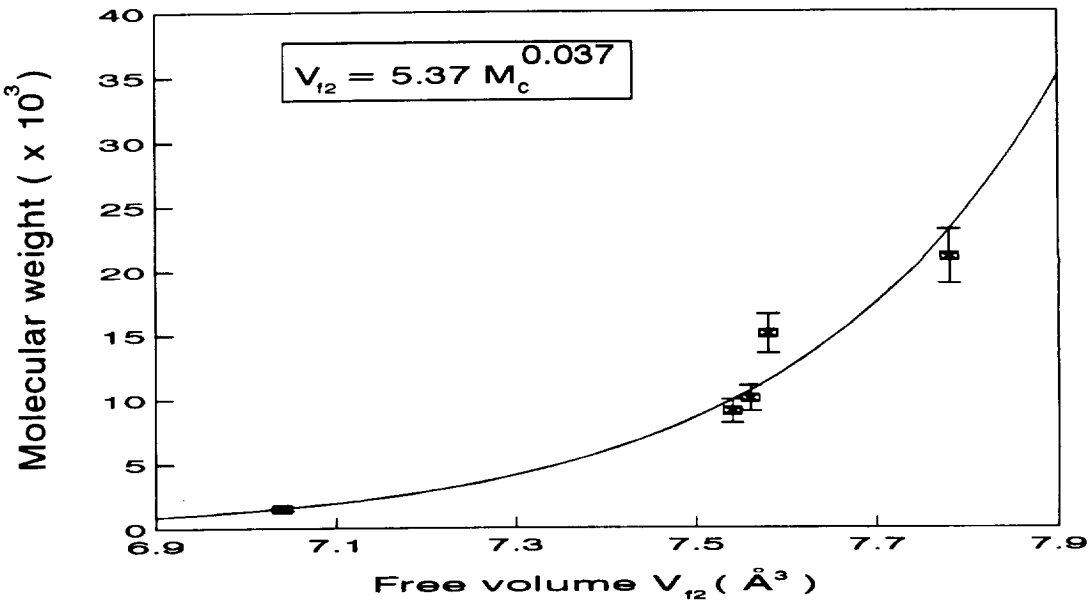

Fig.2. Correlation between Free volume and segmental molecular weight in the test samples.

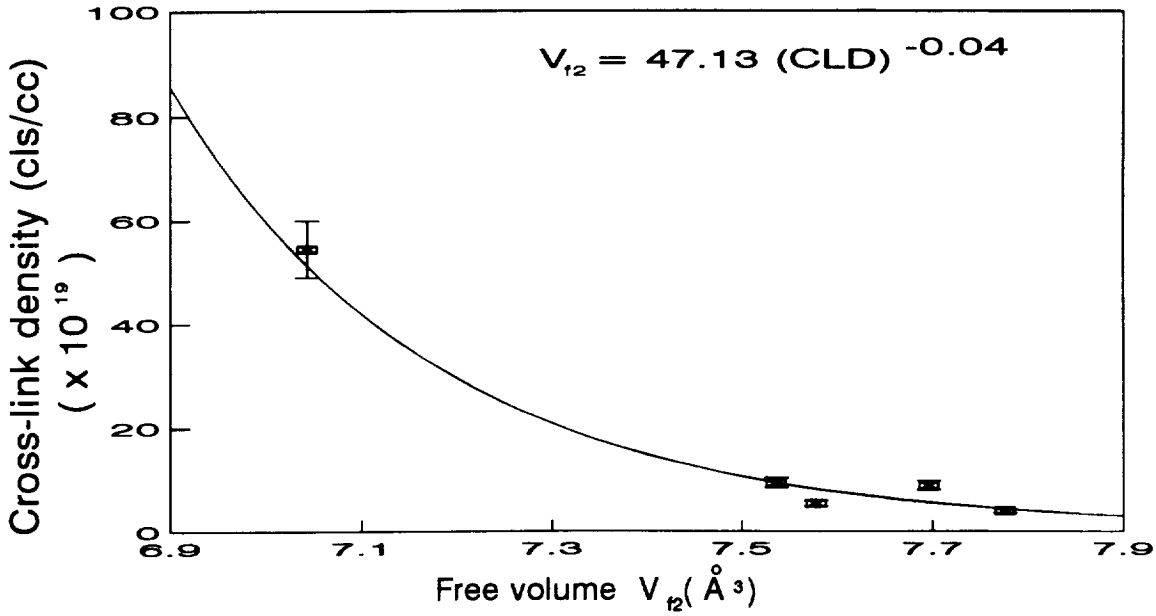

Fig.3. Correlation between Free volume and Crosslink density of the test samples

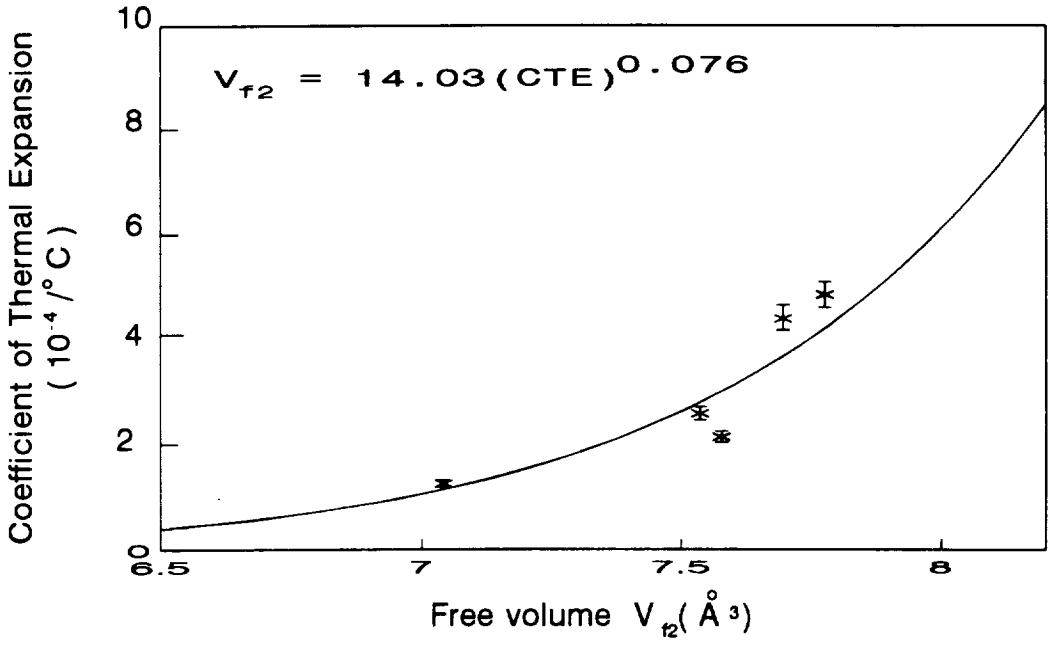

Fig.4. Correlation between Free volume and Coefficient of Thermal Expansion of the test samples.

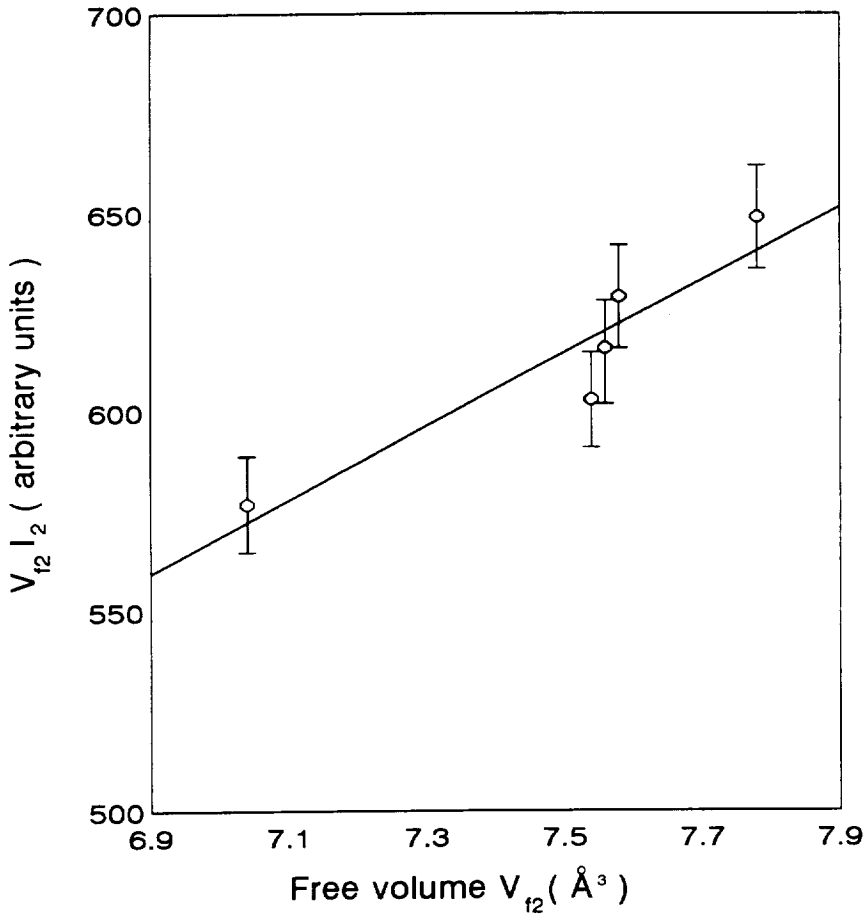

Fig.5. Product of V_{f2} and I_2 as a function of Free volume in the test samples.